

A STUDY OF METHODS OF EXTRACTION AND
DETERMINATION OF THE AVAILABLE
NUTRIENTS IN SOILS

BY

CHING-KWEI LEE

B.S., Fuh-Tan University, 1933

M.S., University of Illinois, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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A STUDY OF METHODS OF EXTRACTION AND DETERMINATION OF THE AVAILABLE NUTRIENTS IN SOILS

INTRODUCTION

The accurate measurement of the amounts of available nutrients in soils is highly desirable when the amount present in the soil is to be correlated with crop growth and responses to added fertilizers. Without a sufficiently accurate measurement, good correlations cannot be expected. Many factors affect the accuracy of these measurements especially when "rapid" or "quick" methods are used. Some of these are concerned with the preparation of the sample and with the extraction of the nutrients from the soil itself, like the magnitude of the exchange capacity, the nature of the clay, or the form of the available nutrient present. Other factors affect the measurement of the extracted nutrients, such as interfering elements or the dilution of the nutrient in the extract.

The problem as it presents itself can be stated as follows: To be of value, soil tests must extract and measure the *total* amount (or a relative proportion) of the available forms of the nutrients in soils so that the amounts present can be correlated with crop growth and response to added fertilizers.

Because many different methods have been suggested for the rapid measurement of the available nutrients in soils, it was considered desirable to study those already suggested as well as new methods, in order to see how they are affected by the kind of factors already mentioned. The fact that most of the methods suggested have not originally been subjected to a critical survey from this viewpoint, yet are being used in practice as tests for available nutrients in many regions, makes this study of special importance.

MATERIALS AND METHODS

The experiment field soils selected for the study represent a variety of soil types, fertility, treatments and responses to fertilization. They have texture ranging from sand to silty clay, pH value 4.5 to 6.4, exchangeable capacity 2.76 m.e. to 35.50 m.e., available phosphorus 26 to 344 pounds per acre, and exchangeable potassium 52 to 457 pounds per acre.

Extracting solutions used for soil testing can be classified into three groups: (1) Mineral acid solutions, represented by 0.3 N HCL as recommended by Baver and Bruner. (2) Salt solutions buffered by weak acids, as represented by approximately 0.75 N sodium acetate solution (10% hydrated sodium acetate), buffered to a pH of 4.8 by acetic acid, originally suggested by Morgan. (3) Concentrated salt solutions, unbuffered. Solutions of this kind were proposed for the available potassium determination by Bray and are represented by a 23% NaNO_3 solution.

Results of calcium, magnesium, manganese and potassium are run by rapid methods compared with those obtained by leaching successively with normal ammonium acetate solution to a 1: 40 soil-solution ratio. The phosphorus rapid test values are compared with the 0.1 N HCL-0.03 N NH_4F extracting method, suggested by Bray for measuring both acid-soluble and absorbed phosphorus.

The effect of drying on the results of exchangeable potassium were studied separately. Samples were collected from the field in a moist condition. Their exchangeable potassium were determined at various drying stage. The effect of moistening on the exchangeable potassium in air-dried samples was also studied.

RESULTS AND CONCLUSIONS

Present studies show that the hydrogen ion in a 0.3 N HCL solution is strong enough to extract almost all the exchange-

able bases, even when the exchange capacity of the soil is high, when a soil-solution ratio of 1:2 is used with a two-minute shaking period.

However, with a salt of a strong base and strong acid, a solution much more concentrated is needed and a 23% solution of NaNO_3 or NaClO_4 , while satisfactory for practical use, is still slightly inefficient with soils very high in base-exchange capacity.

The same sodium concentration with around half of the sodium perchlorate replaced by sodium acetate has a lower extracting ability while sodium acetate itself, even with acetic acid added, is not efficient at the 1:2 ratio. However, at a 1:5 ratio a solution of 10% NaAc and 3% acetic acid is fairly satisfactory.

These findings show that the concentration and nature of the accompanying anion, the magnitude of the exchange capacity, and the ratio of soil to extracting solution are important factors in extracting the exchangeable cations from soils.

Acetates are too poorly ionized to be efficient extractants and the required efficiency has to be obtained, for the 10% solutions of sodium acetate, by adding $2\frac{1}{2}$ times as much solution as is required with the 0.3 N HCl or the 23% NaNO_3 or NaClO_4 solutions.

This dilutes the extracted potassium and makes its determination less accurate in deficient soils containing only 20 to 40 ppm of exchangeable potassium or magnesium. Although 0.3 N HCl is highly efficient, it dissolves out sufficient iron and aluminum from many soils to interfere with the running of the potassium test. These ions must then be removed before determining potassium.

A concentrated neutral solution of a salt of a strong base and strong acid appears, therefore, to meet most nearly the requirements for a useful quick test for the exchangeable (available) bases, especially where one has no other objective,

such as the determination of phosphorus in the filtrate. It is suggested that extracting solutions of this nature for exchangeable bases now being used might be improved by either using a concentration higher than 23% or using a 1:3 ratio because it is believed that the test as now used for exchangeable potassium is sufficiently accurate to give satisfactory results with a slightly wider ratio.

The extraction of the different forms of available phosphorus by quick test techniques is a more difficult problem than extracting the exchangeable bases. More than one available form is present, perhaps several. Their chemical properties vary and so the availability to the plant varies. Theoretically, one should at least measure the acid-soluble and the adsorbed forms separately so that the effectiveness of the combined amounts can be evaluated, but this means running at least two tests on each sample.

The acid concentration and the fluoride concentration in the reference method were originally adjusted so that the phosphorus forms would be extracted in proportion to their availability to plants. The total amounts of each are not extracted. The resulting test values correlate closely with crop responses to phosphates.

Because of the active anionic property of the hydroxide ion, 0.1 N NaOH solution is suggested for the determination of adsorbed phosphorus. An NaOH-HCl extracting procedure for both adsorbed and acid-soluble phosphorus is recommended. The soil is shaken with 0.1 N NaOH in 1:5 ratio for 2 minutes in a test tube, and an equal volume of 0.3 N HCl is added subsequently to the same tube which is again shaken for 2 minutes. Phosphate can be determined colorimetrically in the filtrate by the usual manner.

In none of the suggested methods was the attempt made to recognize the existence of the adsorbed form or its properties except the reference test method, the test for adsorbed phosphorus, and the new test using NaOH and HCl success-

ively. This latter test gives results very similar to the reference method, the reagents are simpler and it may be possible to combine it with a salt for extracting potassium.

All of the other phosphorus methods which employ only acids are inadequate for general use. The ones containing sodium acetate and acetic acid were not sufficiently efficient for phosphorus even in the sandy soils. The ones containing mineral acids are fairly efficient for soils whose phosphorus is mainly in the acid-soluble form, as on the limed plots and where rock phosphate was added, but fail to extract the adsorbed phosphorus effectively on the acid soils high in adsorbed phosphorus.

It would be highly desirable to be able to run all soils for all determinations in soil testing with one extract. Much time and expense would be saved. The findings show that an extractant for this purpose would need certain properties. It would have to be concentrated enough in acid or salt to extract a very high proportion of the exchangeable cations on soils which have high exchange capacity. It should be usable at a sufficiently narrow soil-solution ratio so that the tests could be accurately made directly on the extract, without further concentration. It should not be so acid that amounts of iron and aluminum are removed larger than can be taken care of by modifying the testing techniques, as was done by the writer, by using sodium acetate in the alcohol reagent. Also none of the reagents should interfere with the phosphorus test.

For phosphorus it must be strong enough in acid to dissolve a suitable proportion of the acid-soluble forms and high enough in a replacing anion to replace a good proportion of the adsorbed phosphate at the soil-solution ratio used. But the acid solution must not be strong enough to affect the potassium test through iron and aluminum interference, as already discussed, and the replacing anion must not interfere with the phosphorus test.

The importance of properly drying the soil sample before

determining potassium in Illinois soils is brought out by the results secured. When a soil of high natural potassium fertility, up to 200 lbs./acre, is sampled in moist condition, and its exchangeable potassium is determined before it is air-dried, usually only 40 to less than 10 lbs./acre of potassium can be found. This is at least true of the prairie soils of northern Illinois. The only tests which correlate with crop responses are those secured on thoroughly air-dried soils. The results show that it is the removal of about the last one percent of water removed by air-drying that is most important in securing accurate results for potassium. The data also strongly indicate that it is the clay mineral which is mainly concerned, probably the illite portion. It is suggested that a rearrangement between exchangeable hydrogen on the exchange surface and potassium on interior of the weathered lattice close to the surface takes place during drying. This is the first study of this phenomenon to be reported.

When an air-dried soil sample is moistened with water, and kept in a moist condition, the amount of exchangeable potassium was found to markedly decrease after 3 months. This reversibility of the exchangeability of potassium in soil clay in the moist and air-dried conditions is another interesting phenomenon which needs to be studied further.

The use of an active charcoal during extraction gave an unexpected result. An expected result was that it did keep humus from being extracted, but it greatly increased the amount of iron and manganese extracted although not of the aluminum. It appears that the active charcoal used had a certain limited amount of reducing activity which can reduce iron and manganese to more soluble states and increase the amount extracted. Unless the original forms of these nutrients are available forms, this is objectionable. But if the forms being reduced are available forms this activity of the charcoal would be an advantage.

VITA

The writer was born on the 12th. of February 1912 in Ningpo, China. He graduated in the Department of Chemistry of Fuh-Tan University, Shanghai, China, in December, 1933.

In 1934, he joined the Soils Division of the Geological Survey of China, doing both laboratory and soil survey work. He was in charge of the Soils Division of the Survey during the years 1941-1945. He matriculated at the University of Illinois in October, 1945, and obtained his Master of Science degree in Agronomy in July 1946.

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He has published the following papers:

- 1935. Sodium hydroxide as a substitute for iodine in Robinson's sulphur dioxide method. *Jour. Chinese Chem. Soc.* Vol. 3, 288-292.
- 1939. Determining organic matter in paddy soils. *Ind. Eng. Chem., Anal. Ed.* Vol. 11, 428-429.
- 1940. Variations in yield and composition of wheat plant as affected by the time of applying phosphatic fertilizers. *Jour. Amer. Soc. Agron.* Vol. 32, 782-790.
- 1941. Effect of the solubility of phosphate fertilizers on the growth of maize. *Spec. Soil Publ. No. 4, Geol. Surv. of China.*
- 1943. Chemical properties of the great soil groups of China. *Soil Science*, Vol. 55, 343-351.

Besides, he translated the Book "Geography of the Soils of China", written by James Thorp, into Chinese. He also published some regional soil reports and soil maps in Chinese.

